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MEMORANDUM FOR PRS (Contractor Publication)

FROM: PROI (STINFO) 12 April 2002

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-VG-2002-081**
Phillips, Shawn H.; Gonzalez, Rene I., "Hybrid Inorganic/Organic Reactive Polymers for Severe Environment Protection"

National SAMPE Symposium **(Statement A)**
(Long Beach, CA, no date listed) (Deadline: 15 May 2002)

"Hybrid Inorganic/Organic Reactive Polymers for Severe Environment Protection"

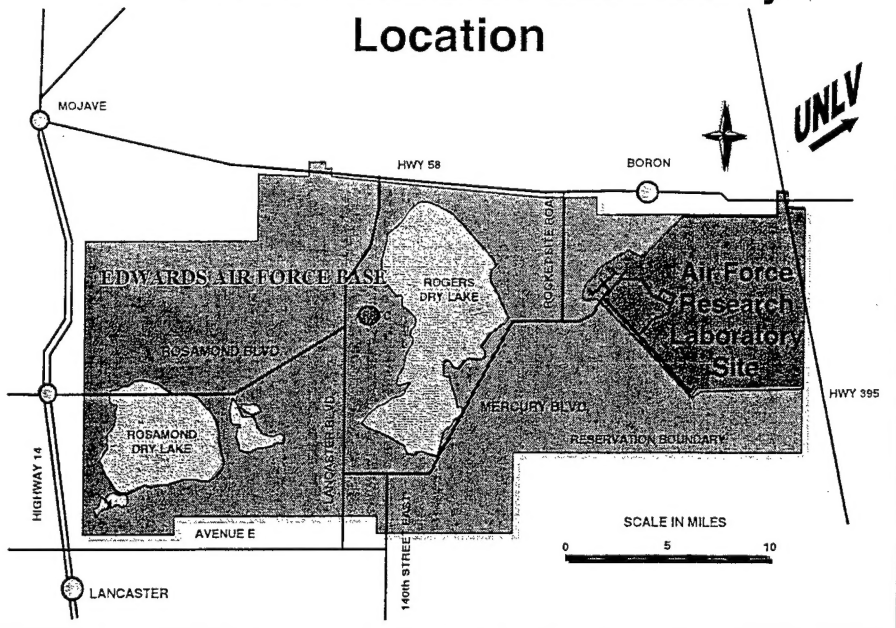
Dr. Shawn Phillips
Chief, AFRL/PRSM
Air Force Research Lab, Edwards

Dr. Wesley Hoffman
Project Leader
High Temperature Comp. Group

Dr. Brent Viers
Project Leader
Polymer Working Group

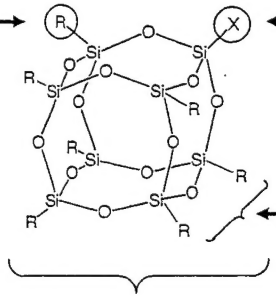
Dr. Jimmy Liu
Project Leader
Fracture Mechanics Group

Air Force Research Laboratory Location



Anatomy of a Polyhedral Oligomeric Silsesquioxane (POSS™) Molecule

Nonreactive organic (R) groups for solubilization and compatibilization.



May possess one or more functional groups suitable for polymerization or grafting.

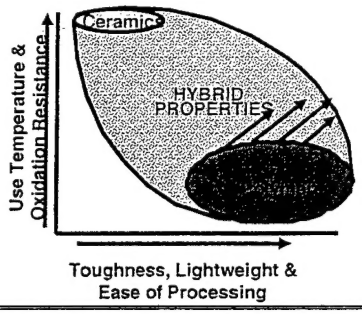
Nanoscopic in size with an Si-Si distance of 0.5 nm and a R-R distance of 1.5 nm.

Thermally and chemically robust hybrid (organic-inorganic) framework.

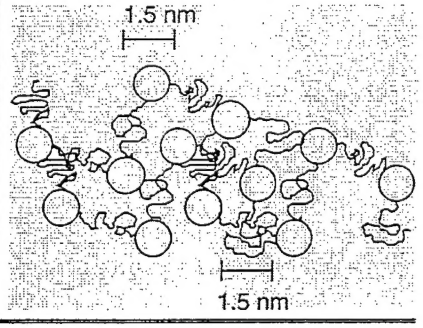
Precise three-dimensional structure for molecular level reinforcement of polymer segments and coils.

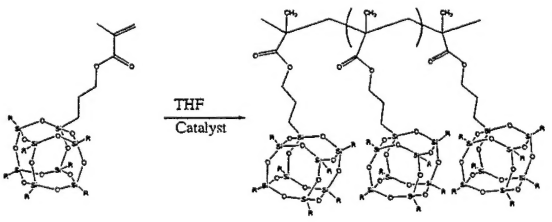
Key Aspects of POSS™ Technology

Hybrid (inorganic/organic) Composition



Nanostructured™ Chemical Reinforcement





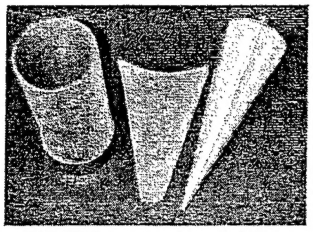
POSS™ technology does not require manufacturers to retool or alter existing processes.

Lichtenhan et. al. *Macromolecules* 1993, *26*, 2141.
Lichtenhan, *Polym. Mater. Encyclopedia* 1996, *10*, 7768.

Solid Propellant Insulation Program

Project Goals 6.2 (IHPRPT)

Case Insulation

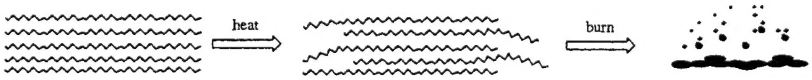


POSS-Insulation Sample

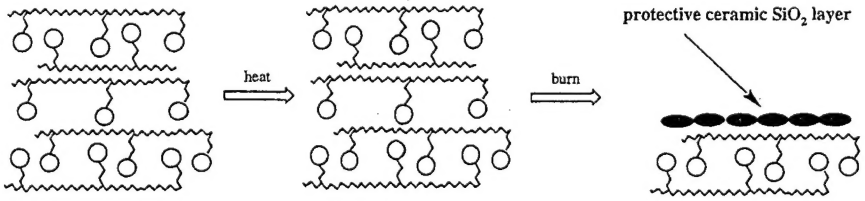
[redacted]

POSS for Ablative Materials

Traditional Polymer

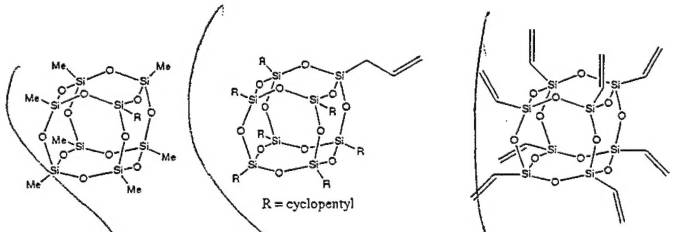


POSS Polymer



The Silicon to Oxygen ratio of 1:1.5 is the key!!!

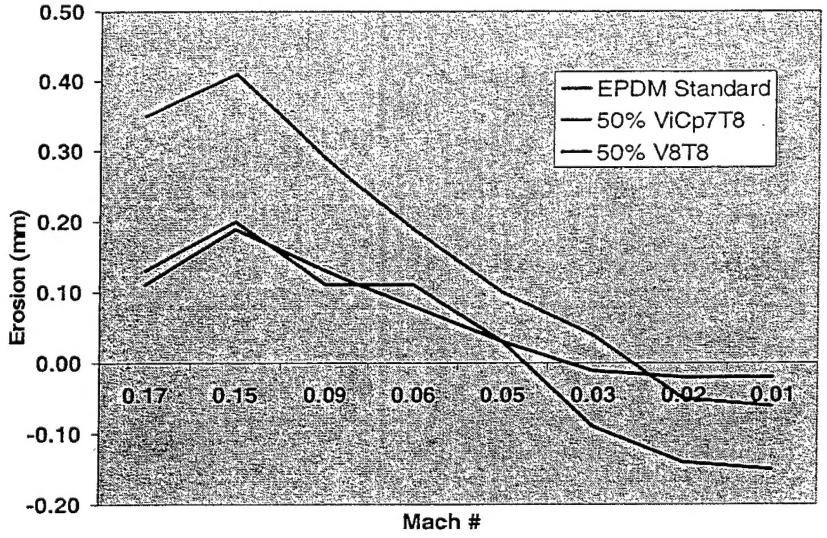
Comparisons of POSS in EPDM



At 50 wt% loadings relative to a proprietary base-line material

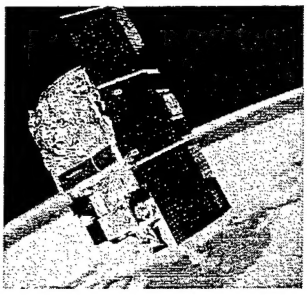
Hardness:	15%↑	no change	17%↑
Tensile:	5%↓	27%↓	1%↓
Elongation:	no change	no change	no change
Viscosity:	35%↓	21%↓	36%↓
Density:	15%↑	3% ↓	12%↑

Convergent Cone SRM Insulation Tests



Negative numbers represent formation of structural char

Goal: Develop Multi-Functional, Space-Resistant Materials



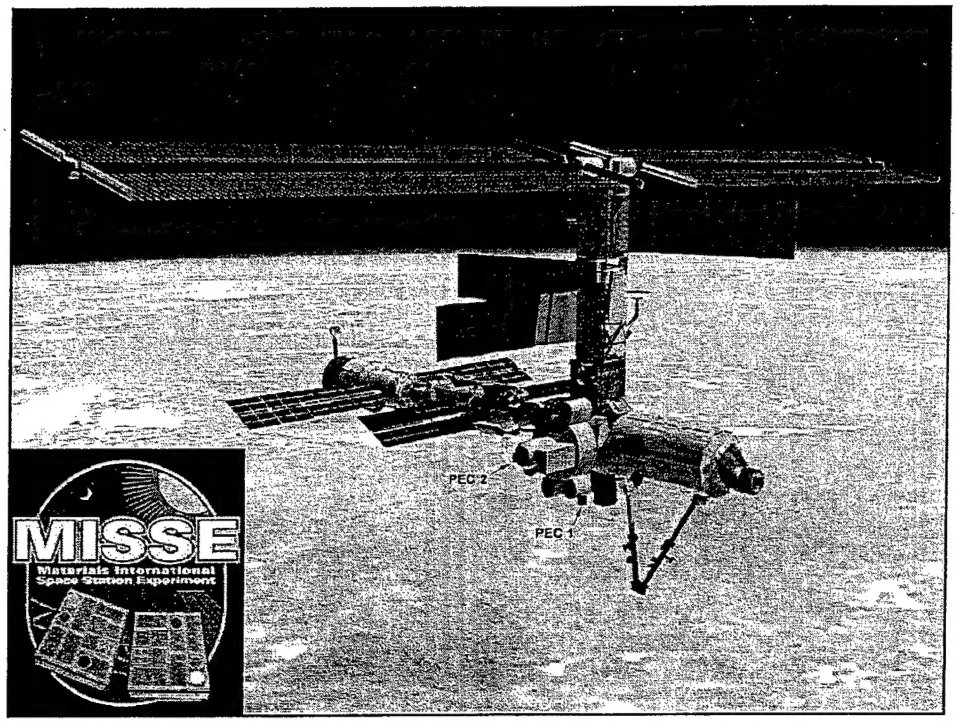
Satellites & Space Systems

Bond	Dissociation Energy (EV)	λ (nm)	Material
$-C_6H_4-C(=O)-$	3.9	320	Kapton®
C-N	3.2	390	Kapton®
CF_3-CF_3	4.3	290	FEP Teflon®
CF_2-F	5.5	230	FEP Teflon®
Si-O	8.3	150	Nanocomposite
Zr-O	8.1	150	Nanocomposite
Al-O	5.3	230	Nanocomposite

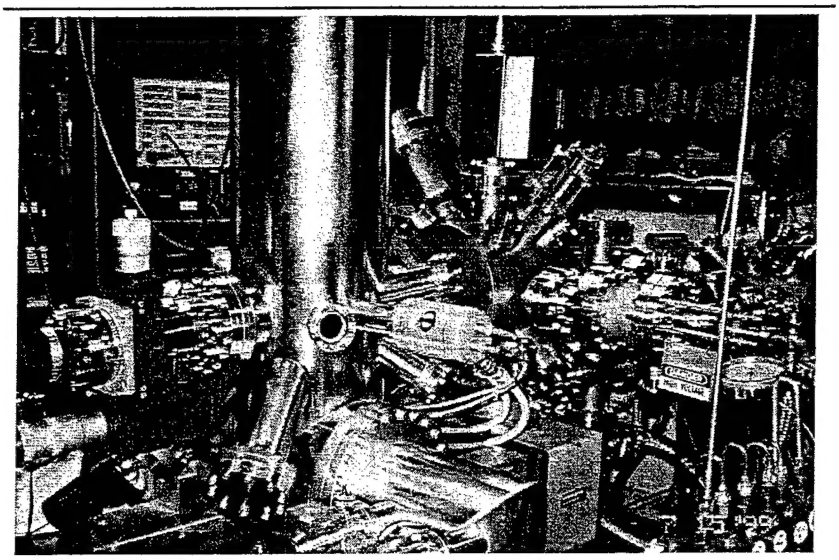
Objectives

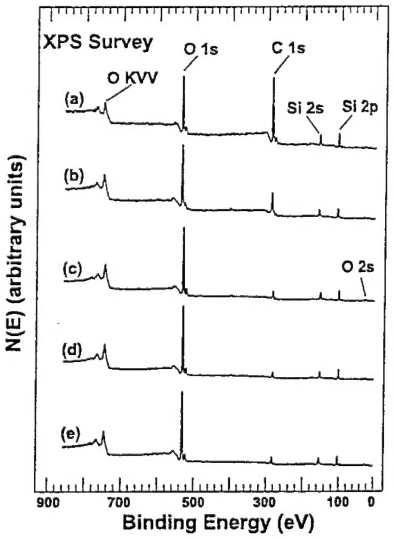
- Increase Space Resistance (AO, particle & VUV radiation, thermal cycling) of Polymeric Materials

- Self-Passivating/Self-Rigidizing/Self-Healing based on organic/ inorganic nanocomposite incorporation

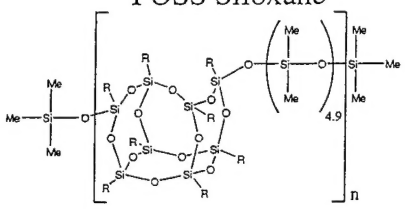


UF LEO Simulation Facility



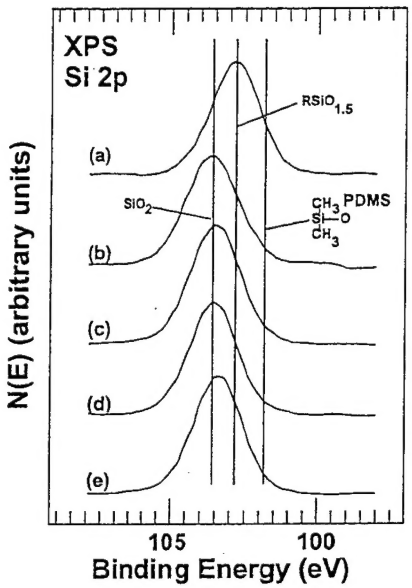


POSS Siloxane



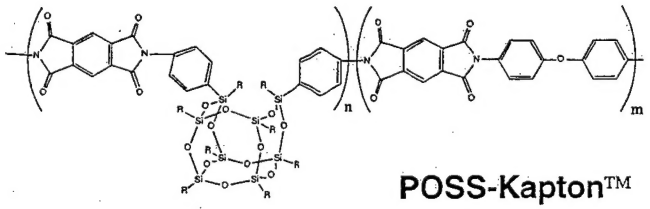
Sample Treatment	O	C	Si
As entered	18.5	65.0	16.6
2.0 hr	33.8	48.4	17.8
24.6 hr	49.1	22.1	28.8
63.0 hr	55.7	16.3	28.0
4.8 hr air	52.8	19.5	27.7

XPS survey spectra obtained from a solvent-cleaned, POSS-PDMS film (a) after insertion into the vacuum system, (b), after a 2-hr (c) 24.6-hr and (d) 63-hr exposure to the hyperthermal AO flux, and (e) 4.75-hr air exposure following the 63-hr AO exposure.



High Resolution Si 2p spectra obtained from a solvent-cleaned, POSS-PDMS film (a) after insertion into the vacuum system, (b), after a 2-hr (c) 24.6-hr and (d) 63-hr exposure to the hyperthermal AO flux, and (e) 4.75-hr air exposure following the 63-hr AO exposure.

New POSS-Polymers

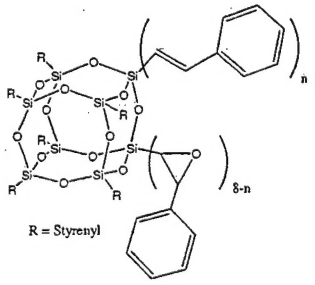


POSS-Kapton™

Goal: Determine if POSS incorporation into high-performance polymers will improve SOTA systems.

Have Targeted Four Polymer Systems:

- POSS-Polyimides
- POSS-Epoxies
- POSS-Polyphenylenes
- POSS-Polycarbonates

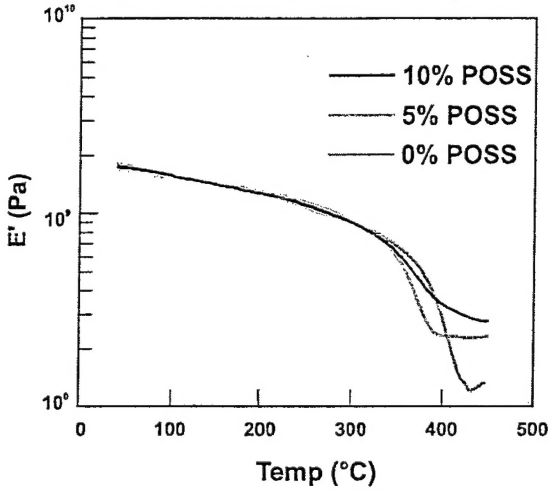


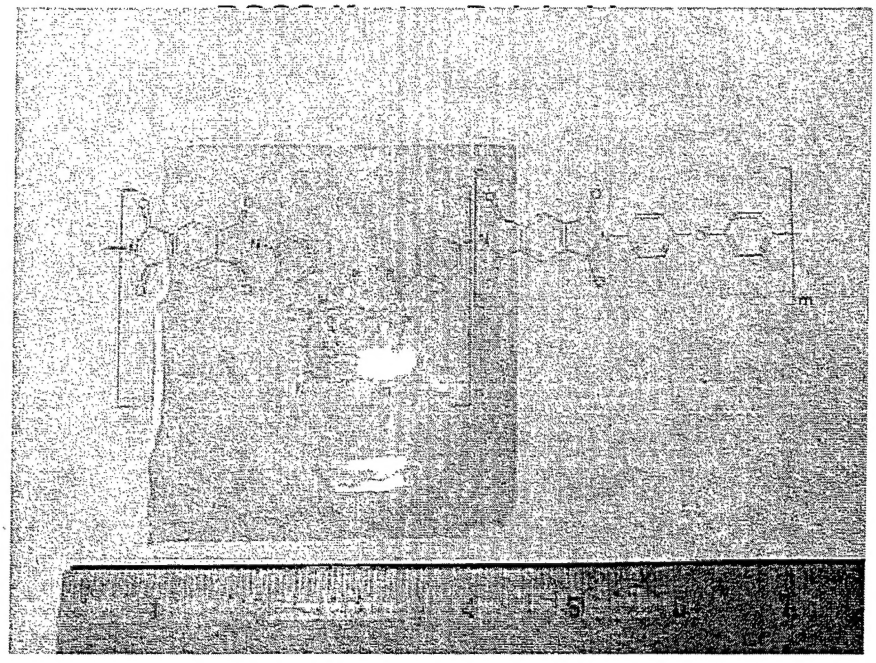
R = Styrenyl

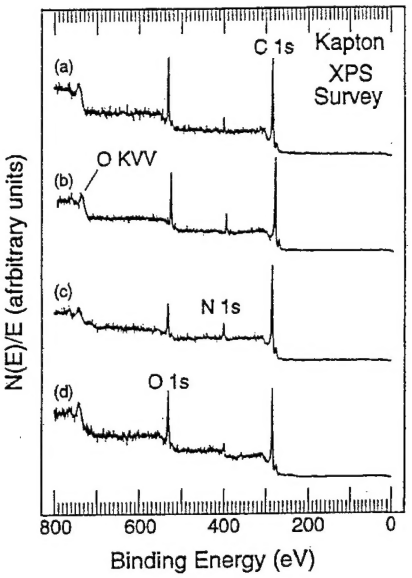
Mechanical Analysis - POSS Kapton™

DMTA Experiments

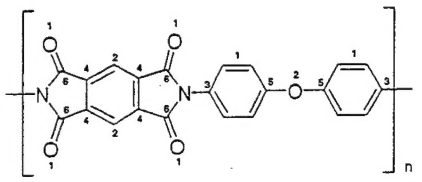
0,5, and 10 wt % POSS in Kapton







Kapton



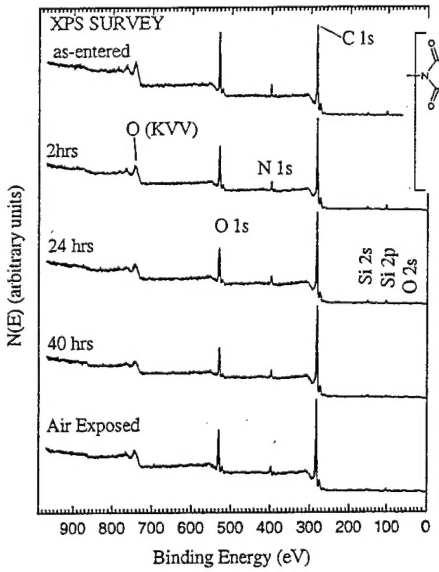
Composition, at %

Sample Treatment	O	C	N
As entered	18.1	77.7	4.2
2.0 hr	14.4	78.4	7.2
24.6 hr	9.2	83.2	7.8
3 hr in air	17.9	78.2	3.9

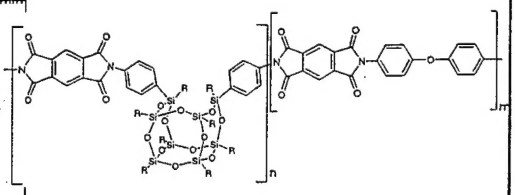
Grossman, E.; Wolan, J.T.; Mount, C.K.; Hoflund, G.B.; J. Spacecraft and Rockets, 36, No. 1, 75-78

XPS survey spectra obtained from a solvent-cleaned, Kapton film after (a) insertion into the vacuum system, (b) a 20-min, and (C) a 24-h exposure to the hyperthermal AO flux, and (d) a 3-hr air exposure following the 24-hr exposure.

10 wt% POSS Kapton Polyimide

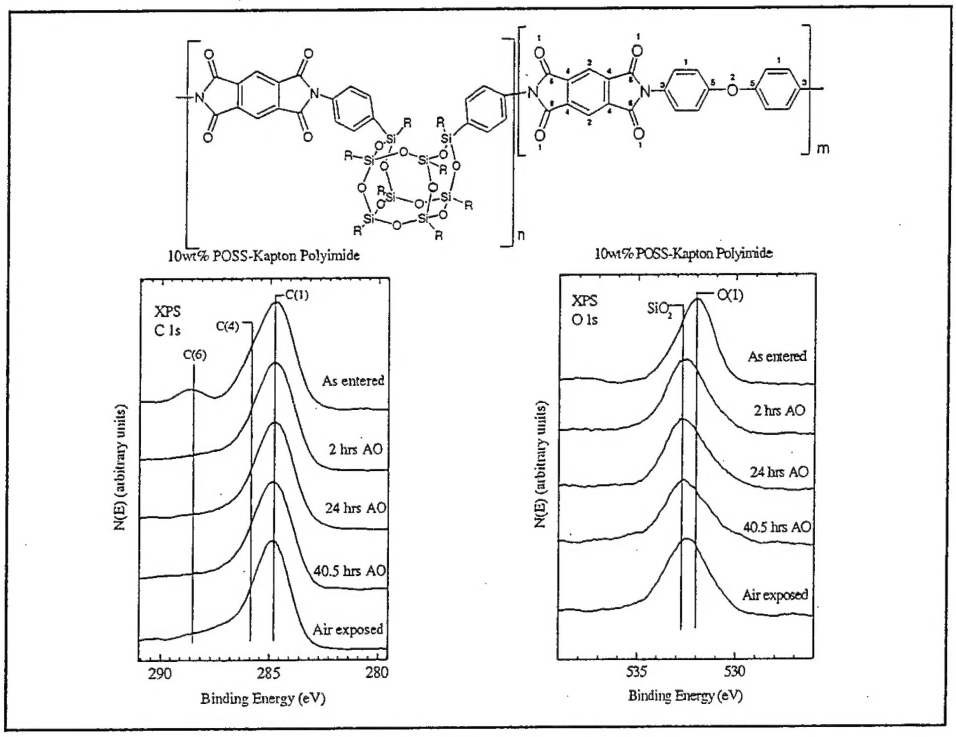


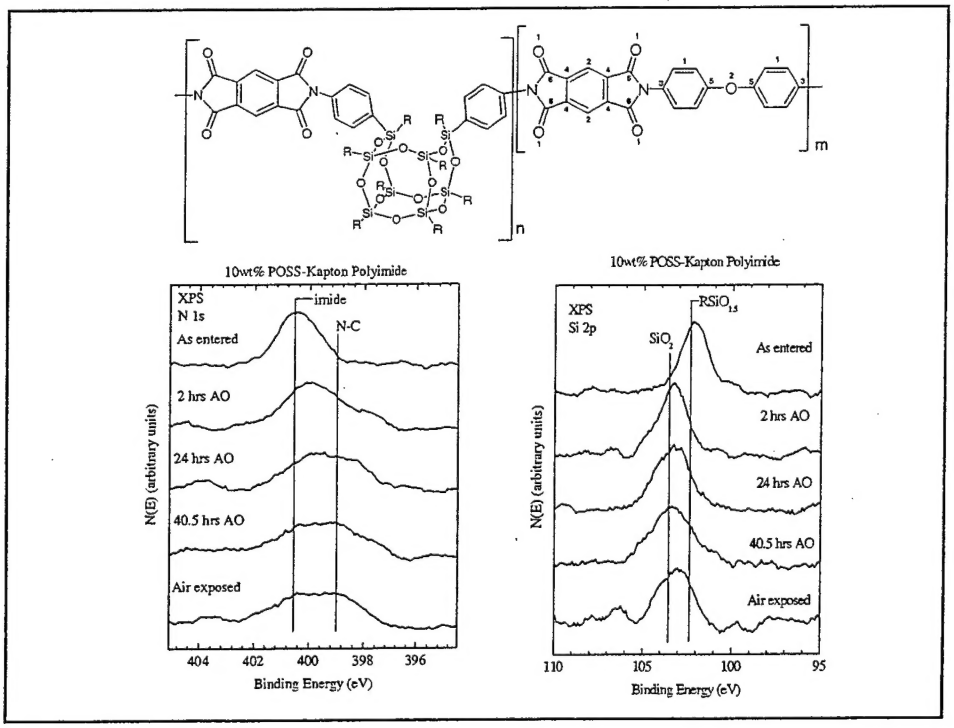
10 wt% POSS Kapton



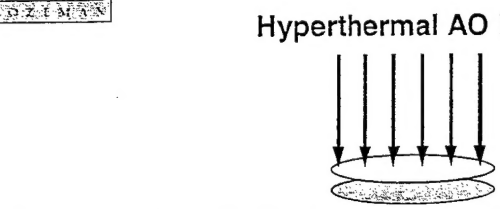
Composition, at %

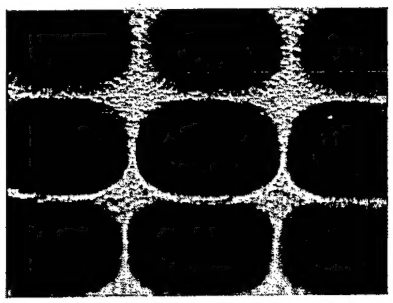
Sample Treatment	O	C	N	Si	O/Si
As entered	15.9	74.5	4.9	4.6	3.4
2.0-hr	14.3	72.6	8.2	4.9	2.9
24.0-hr	11.1	79.6	4.9	4.4	2.5
40.0-hr	9.1	81.5	5.6	3.7	2.4
Air exposed	13.9	76.8	5.8	3.5	3.9


10wt% POSS-Kapton Polyimide
XPS
C 1s
C(1)
C(4)
C(6)
As entered
2 hrs AO
24 hrs AO
40.5 hrs AO
Air exposed
N(E) (arbitrary units)
290
285
280
Binding Energy (eV)
10wt% POSS-Kapton Polyimide
XPS
O 1s
SiO2
O(1)
As entered
2 hrs AO
24 hrs AO
40.5 hrs AO
Air exposed
N(E) (arbitrary units)
535
530
Binding Energy (eV)

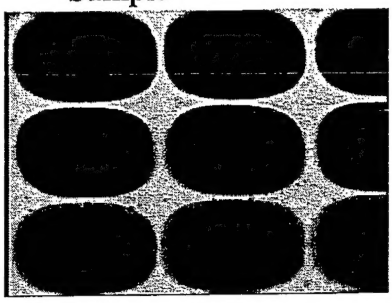

10wt% POSS-Kapton Polyimide
XPS
N 1s
imide
N-C
As entered
2 hrs AO
24 hrs AO
40.5 hrs AO
Air exposed
N(E) (arbitrary units)
404
402
400
398
396
Binding Energy (eV)
10wt% POSS-Kapton Polyimide
XPS
Si 2p
SiO2
RSiO1.5
As entered
2 hrs AO
24 hrs AO
40.5 hrs AO
Air exposed
N(E) (arbitrary units)
110
105
100
95
Binding Energy (eV)

Surface Topographical Analysis/Profilometry





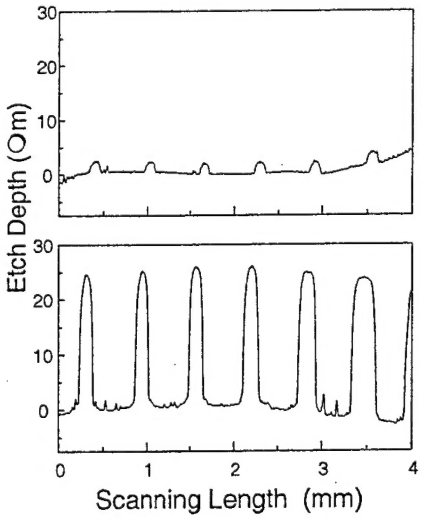
Kapton H



Kapton 10 wt% POSS

O-Atom Etching Experiment

8.47×10^{20} atoms cm^{-2}



Kapton 10 wt% POSS
$R_e = 2.56 \times 10^{-25}$

Average etch depth:
2.2 Om

Kapton H Standard
$R_e = 3.00 \times 10^{-24}$

Average etch depth:
25.4 μm

SUMMARY

Significant advances in materials and processing technologies have been made within AFRL/PRSM

- demonstrated ceramic char layer of POSS-insulation
- synthesized POSS-Kapton (up to 20 wt% POSS)
- demonstrated significant (9x) atomic oxygen survivability and formation of ceramic SiO2 layer

Basic (6.1) and Applications (6.2) research have been successfully integrated in Air Force Propulsion Programs

- successful technology transfer of POSS nanotechnology
- POSS nanotechnology on critical and high risk path for the Air Force

Materials Applications Branch is willing/eager to transition technology (CRADA's, SBIR's, DUS&T's, Academic Collaborations, etc...)

ACKNOWLEDGEMENTS

Capt Rene Gonzalez, Ph.D., Prof. Gar Hoflund

AFRL/PRSM: Dr. Brent Viers, Dr. Tim Haddad, Dr. Rusty Blanski, Dr. Steve Svejda, Pat Ruth, Brian Moore, Justin Leland

Major

Hybrid Plastcs: Dr. Joe Lichtenhan and Dr. Joe Schwab

All the academic collaborators: Profs Frank Feher, Andre Lee, Pat Mather, Ben Hsiao, Mike Bowers, Rick Laine, Bryan Coughlin, Steve Nutt, etc.

Industrial/Government Collaborators

$$AFRL & AFOSR$$